



## Kinetic study of the oxidation of hydrogen sulfide by Fe(III)-Tes=trapolypophosphate (TPP) and Fe(II)-TPP by O<sub>2</sub>



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### ABSTRACT

Tetrapolyphosphate (TPP) forms complex with iron(III) (Fe(III)-TPP), which is a highly stable catalyst for the air/O<sub>2</sub> oxidation of HS<sup>−</sup> in both the buffered and non-buffered solutions. The first step in this process is formation of the Fe(III)(HS<sup>−</sup>)TPP complex followed by an electrontransfer from HS<sup>−</sup> to Fe(III) and formation of Fe(II)TPP and HS<sup>•</sup>. The electron transfer process depends on the half-wave potential ( $E_{1/2}$ ) of the complex. The  $E_{1/2}$  of Fe(III)/(II)TPP was measured electrochemically and it was found to decrease from 0.061 to −0.14 V vs. SHE (standard hydrogen electrode) with increasing solution pH from 4 to 9. The oxidation of Fe(II)TPP by O<sub>2</sub> is shown to follow a four-step reaction mechanism, and the reaction kinetic parameters were calculated using experimental data. The second-order rate constant of the reaction between Fe(III)TPP and HS<sup>−</sup> at pH 9 was found – within 95% confidence limit – to be about  $30.5 \pm 21.0 \text{ M}^{-1} \text{ s}^{-1}$ . This study provided valuable information about the oxidation characteristics of Fe(II)TPP by O<sub>2</sub> and the capability of Fe(III)TPP as a catalyst for the air/O<sub>2</sub> oxidation of HS<sup>−</sup>.

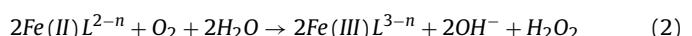
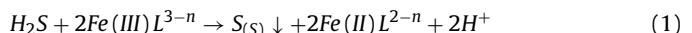
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### 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) ( $\text{pK}_{\text{a}1} = 6.9$ ) is extremely toxic and irritating, existing mainly as HS<sup>−</sup> in water at pH > 7 [1,2]. H<sub>2</sub>S has a permissible exposure limit of 20 parts per million by volume (ppmv) and regulated by the Occupational Safety & Health Administration (OSHA, USA). Inhalation of 500–1000 ppmv of H<sub>2</sub>S will cause rapid loss of consciousness and death through respiratory paralysis and asphyxiation [3]. Therefore, the amount of H<sub>2</sub>S must be reduced to acceptable levels before the discharge of a flue gas due to safety and environmental concerns.

Economical removal of H<sub>2</sub>S from the industrial streams is not easy, and many processes have been proposed and tested for this purpose [4]. Desulfurization by the liquid redox sulfur recovery (LRSR) process with iron(III)-chelate – Fe(III)-L; L = ethylenediaminetetraacetate (EDTA), nitrilotriacetate, and other amniopolycarboxylate – catalysts [4,5] have attracted a lot of attentions from both industry and academic researchers over the last several decades. In this process, H<sub>2</sub>S is catalytically oxidized according to Eq. (1) to elemental sulfur by Fe(III)-L. The Fe(II)-L

produced in reaction (1) reacts with oxygen (O<sub>2</sub>) and oxidizes to Fe(III)-L (Eq. (2)) [6].



where n denotes the charge of organic ligand L. Researchers revealed that NTA is the best ligand investigated so far for the desulfurization process due to its high efficiency, stability and low cost of NTA [7–9].

The hydrogen peroxide generated in Reaction (2) reacts with Fe(II)L<sup>2-n</sup> and generates hydroxyl radical (•OH), which in turn reacts very fast with the ligand and initiates a cascade of reactions that leads to the degradation and loss of the catalyst [10–13]. This is one of the major drawbacks of the Fe(III)-L catalysts. Attempts have been made to prevent the decomposition of catalysts by using •OH scavengers [11,12,14] or employing chelating agents that are more resistant to •OH attack [12,15,16]. These strategies increase the useful life of the catalysts but do not prevent their degradation.

Polyphosphates (PP) form stable complexes with Fe(III) – Fe(III)-PP – and are not oxidized readily by •OH. As a result, Fe(III)-PP were found to be very stable when used to catalyze the air/O<sub>2</sub> oxidation of H<sub>2</sub>S and act as true catalysts [12]. For example, it has been shown that [12] approximately 34% of 5 mM Fe(III)NTA was destroyed in catalyzing the oxidation of 115 mM H<sub>2</sub>S in pH 9 borate buffer solution, and the fraction degraded reached 100%

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in unbuffered solution; while, very little, if any, degradation of Fe(III)TPP(tetrapolyphosphate) was found to occur under similar conditions.

In the practical desulfurization process, the rate of regeneration of Fe(III)-L complex is slow compared to its rate of reduction in Eq. (1), making the second step (Eq. (2)) the rate limiting step [5]. Brown and Mazarella (1987) have shown that the oxidation of Fe(II)L by O<sub>2</sub> proceeds according to the following reactions.



Applying steady-state approximation for the intermediate superoxide ion, O<sub>2</sub><sup>•-</sup>, the rate of the oxidation of Fe(II)L can be expressed by the following equation (Eq. (6)).

$$\frac{d[Fe(II)L]}{dt} = \frac{4k_1 k_2 [O_2(\text{soln})][Fe(II)L]^2}{k_{-1}[Fe(III)L] + k_2[Fe(II)L]} \quad (6)$$

Integration of the above differential equation leads to the following equation.

$$\begin{aligned} \frac{(k_{-1} - k_2)}{k_{-1}(1+R)} \ln \frac{[Fe(II)L]}{[Fe(II)L]_0} + \frac{[Fe(II)L]_0 - [Fe(II)L]}{[Fe(II)L]} \\ = \frac{4k_2 K_{eq} [O_2(\text{soln})]}{(1+R)} t \end{aligned} \quad (7)$$

where k<sub>1</sub>, k<sub>-1</sub>, and k<sub>2</sub>, denote the reaction rate constants between Fe(II)L and O<sub>2</sub>, Fe(III)L and O<sub>2</sub><sup>•-</sup>, and Fe(II)L and O<sub>2</sub><sup>•-</sup> respectively, K<sub>eq</sub> = k<sub>1</sub>/k<sub>-1</sub> and R = [Fe(III)L]<sub>0</sub>/[Fe(II)L]<sub>0</sub>.

We have shown in the previous paper [12] that Fe(III)-PP can act as true catalysts for the LRSR process and elucidated the mechanism of air/O<sub>2</sub> oxidation of H<sub>2</sub>S catalyzed by Fe(III)-PP. This paper presents the results of our investigations on: a) the effect of solution pH on the half-wave reduction potential (E<sub>1/2</sub>) of Fe(III)-TPP, b) the kinetics of O<sub>2</sub> oxidation Fe(II)TPP and present the kinetic parameters, and c) the kinetics of O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III)TPP and derive the kinetic parameters

## 2. Materials and methods

### 2.1. Reagents and solution preparation

All chemicals used in this investigation were reagent grade and were used as received. Sodium sulfide nonahydrate, iron(III) sulfate (97% purity) hydrate, and iron(II) sulfate heptahydrate, were purchased from Sigma Aldrich. Sodium tetrapolyphosphate (Na<sub>6</sub>P<sub>4</sub>O<sub>13</sub>, MW=470 gmol<sup>-1</sup>) was purchased from BOC sciences.

A 0.1 M Fe(III)TPP ([TPP]:[Fe]<sub>0</sub> = 2:1 in mol ratio) stock solution was prepared by dissolving 0.01 mol TPP in 50 mL 18 MΩ MilliQ water (Millipore Corporation) and then slowly adding 0.0025 mol of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> into the solution. A 0.5 M HS<sup>-</sup> stock solution was prepared by dissolving 0.05 mol of sodium sulfide nonahydrate in 100 mL N<sub>2</sub>-saturated MilliQ water. The pH of solutions was adjusted using 0.1 M NaOH and 0.1 M HCl.

### 2.2. Measurement of the oxidation rate of Fe(II)TPP by O<sub>2</sub>

The kinetics of oxidation of Fe(II)TPP by O<sub>2</sub> was carried out in phthalate buffer (pH 4.2, 5, and 5.9), tris buffer (pH 7), and borate buffer (pH 8 and 9). Approximately 150 mL of the buffer solution was added to a 400-mL beaker and mixed using a magnetic stirring bar. The mixing speed was set at 700 rpm and the solution was maintained saturated with O<sub>2</sub> during the reaction. The reaction was initiated by adding 0.5 mM Fe(II)TPP into the solution at time zero.

Samples were taken at different time intervals and analyzed for Fe(II). All reactions were carried out at room temperature (21 ± 0.5 °C).

### 2.3. The air/O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III)TPP

The air/O<sub>2</sub> oxidation of HS<sup>-</sup> (2, 4, 6, and 8 mM) catalyzed by Fe(III)TPP was conducted in pH 9 borate buffer. Approximately 125-mL of the buffer solution was added to a 250 mL Erlenmeyer flask under constant stirring (500 rpm) and spiked with 0.5 mM Fe(III)TPP followed by the addition of a known concentration of HS<sup>-</sup> from a stock solution to initiate the reaction. Samples were taken at different time intervals and analyzed for HS<sup>-</sup> and Fe(II).

### 2.4. Measurement of the half-wave potential of Fe(III)/Fe(II)TPP

Cyclic voltammetry was conducted by a Metrohm Autolab electrochemical workstation using a three-electrode system. Platinum electrode, silver chloride electrode, and glassy carbon electrode were used as counter, reference, and working electrodes, respectively. The electrolyte used in this study was 0.1 M NaCl. Scan rate was 1.2 V/s.

### 2.5. Analytical methods

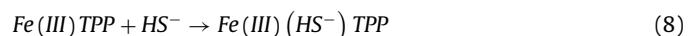
Absorption spectra were recorded employing a Varian Cary® 50 UV-vis spectrophotometer. The spectrum of the mixture of Fe(III)TPP with HS<sup>-</sup> was obtained by adding HS<sup>-</sup> stock solution into the Fe(III)TPP solution and scanning the mixture immediately. The iron concentration was measured using the 1,10-phenanthroline method [17]. The HS<sup>-</sup> concentration was measured by following the HACH Methylene Blue Method 8131 procedures.

## 3. Results and discussion

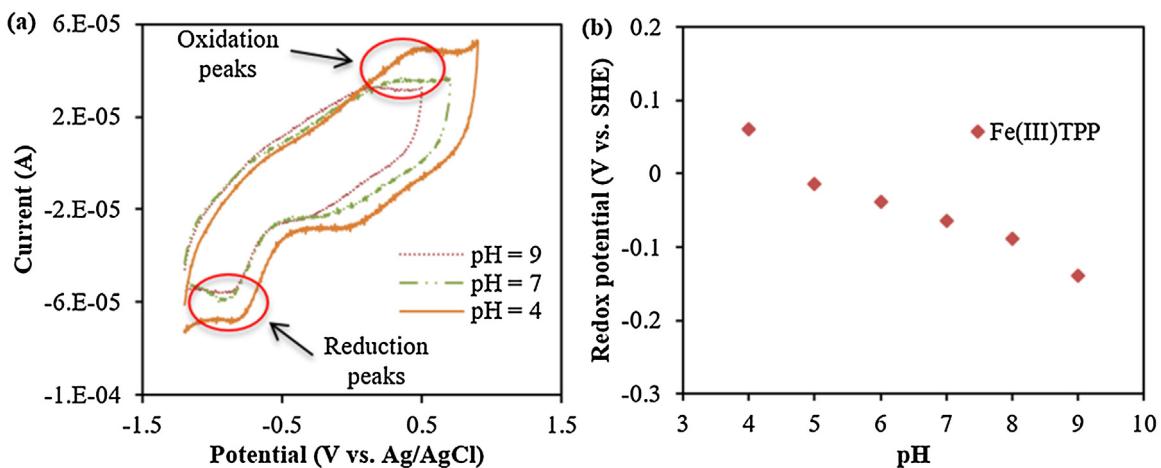
### 3.1. Reduction potential of Fe(III)/Fe(II)TPP and its complexation with HS<sup>-</sup>

It has been shown that the addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to a solution of Fe(III)-EDTA generates a purple colour in alkaline solution [18]. This was subsequently attributed – using x-ray crystallography data – to the presence of a seventh coordination site in the complex, which is loosely occupied by a water molecule [19] and that the water molecule can be replaced competitively by a stronger ligand such as H<sub>2</sub>O<sub>2</sub> [20] and azide (N<sub>3</sub><sup>-</sup>) [21]. The Fe(III)TPP is also believed to contain a seventh coordination site that can be occupied competitively by HS<sup>-</sup>. It is for this reason that the addition of HS<sup>-</sup> to a solution of Fe(III)TPP rapidly generates an intense blue-purple colour that disappears slowly, similar to that reported by Safarzadeh-Amiri, et al. [12]. This blue-purple colour was attributed to the formation of Fe(III)(HS<sup>-</sup>)TPP complex, which absorbs strongly at wavelength above 350 nm and exhibits absorption bands around 414 nm, 513 nm, and 611 nm [12].

The disappearance of the blue-purple colour is accompanied by the appearance of the yellowish elemental sulfur. The first step in this transformation is the transfer of an electron from the sulfide ligand to Fe(III), generating Fe(II)TPP and sulphydryl radical (HS<sup>•</sup>) according to the following reaction [12].



Reaction (9) is irreversible and the sulphydryl radicals (HS<sup>•</sup>, pK<sub>a</sub> < 7.0) generated in this reaction and its conjugated base (S<sup>2-</sup>) dimerize and polymerize rapidly to elemental sulfur and/or oxidize to sulfur oxyanions [12]. The Fe(II)TPP generated in Reaction



**Fig. 1.** a) Cyclic voltammograms of Fe(III)TPP in pHs 4, 7, and 9 buffer solutions ( $[Fe(III)]_0 = 1 \text{ mM}$ , the electrolyte was 0.1 M NaCl scan rate was set at 1.2 V/s), and b) variation of  $E_{1/2}$  as a function of solution pH.

(9) reacts with  $O_2$  and oxidizes back to Fe(III)TPP; as a result, the role of Fe(III)TPP as a catalyst is to transfer electrons from  $HS^-$  to  $O_2$ .

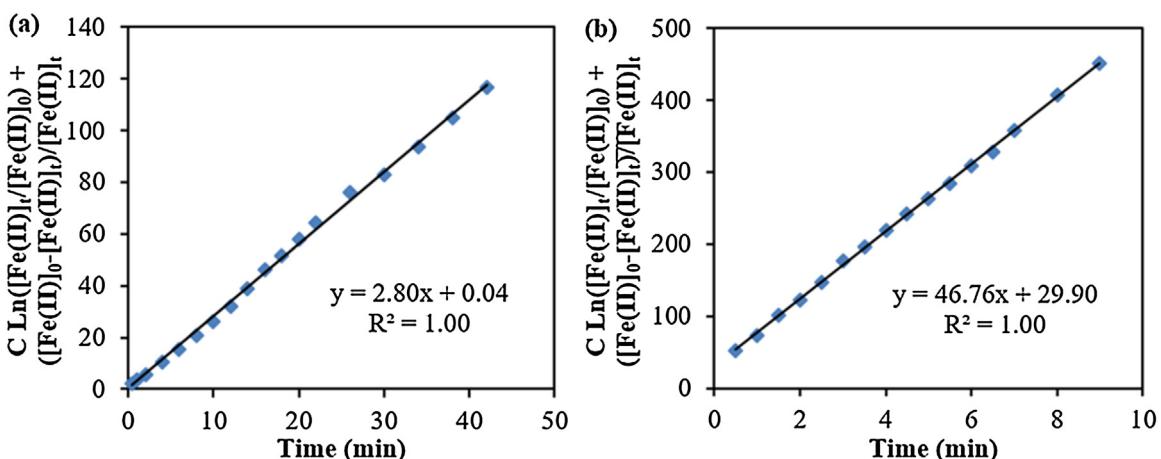
The rate of electron transfer from  $HS^-$  ligand to Fe(III) in the above reaction is directly proportional to the reduction potential of Fe(III)TPP. In order to gain further insight into the catalytic properties of Fe(III)TPP we have measured the redox potential of Fe(III)/Fe(II)TPP in buffered solutions and at different pH.

The cyclic voltammograms of Fe(III)/(II)TPP in pHs 4, 7, and 9 buffer solutions are given in Fig. 1a and additional voltammograms at pHs 5, 6, and 8 are provided in Fig. S1 (Supplementary Material (SM)). The  $E_{1/2}$  values were calculated by taking the average of the potentials at the oxidation and reduction peaks marked with red circles, then converting them from the Ag/AgCl based reference electrode values to the standard hydrogen electrode (SHE) based reference electrode values. The  $E_{1/2}$  values were 0.061, -0.014, -0.039, -0.064, -0.089, and -0.14 V (vs. SHE) at pHs 4–9, respectively. An  $E_{1/2}$  value of -0.046 (vs. SHE) was obtained for Fe(III)TPP from the voltammogram (pH was not specified) provided by Wang et al. [22]. Fig. 1b shows that the  $E_{1/2}$  value of Fe(III)/(II)TPP decreases almost linearly with a slope of about -0.036 with the increase of solution pH, in agreement with previous work on Fe(III)EDTA [23]. The dependence of the  $E_{1/2}$  value on pH is primarily due to hydrolysis of Fe(III)TPP in which the water molecule is replaced with hydroxide ( $OH^-$ ) as the solution pH increases [23].

In the desulfurization process, the redox potential of the catalyst should be high enough to oxidize  $H_2S$  and low enough for the reduced form to be oxidized by  $O_2$ , i.e.,  $E_{S/H_2S} < E_{Fe(III)/(II)L} < E_{O_2/H_2O}$ , which is to say  $-0.21 \text{ V} < E_{Fe(III)/(II)L} < 0.59 \text{ V}$  (Luo, et al. [24]). Generally, the higher the redox potential of a catalyst (“stronger” for the  $H_2S$  oxidation), the more difficult is the regeneration step. This is because as the redox potential becomes more negative (approaching the redox potential of  $O_2$ ), the driving force for the oxidation of the reduced form of catalyst by  $O_2$  decreases. Therefore, catalysts with comparatively higher redox potentials but lower than 0.24 V, the  $E_{1/2}$  ( $S/HS^-$ ), are preferred for the desulfurization process [4] because they can be regenerated faster with  $O_2$ . The chelation of Fe(III) by TPP decreases its redox potential, making the oxidation of Fe(II)TPP by  $O_2$  thermodynamically favorable [25]. With a redox potential in a range of 0.061–0.14 V at pH 4–9, the Fe(III)TPP complex appears to be a suitable catalyst for the air/ $O_2$  oxidation of  $HS^-$ .

### 3.2. Oxidation of Fe(II)TPP by $O_2$

The oxidation of Fe(II)L and regeneration of Fe(III)L is a key step in the practical LRSR process. The rate of oxidation of Fe(II)L by  $O_2$  is influenced significantly by the chelating agents (L), which affects the redox potential of Fe(III)/Fe(II)L. The rate of oxidation of Fe(II)L, but not Fe(II)TPP, by  $O_2$  have been reported in the literature. It is



**Fig. 2.** Kinetic analysis of Fe(II)TPP oxidation by  $O_2$  according to Eq. (7) at pH 4.2 phthalate buffer (a) and pH 8 borate buffer (b) ( $[Fe(II)]_0 = 0.5 \text{ mM}$ ; the term C in the coefficient denotes  $(k_{-1} - k_2)/k_{-1}(1+R)$  in Eq. (7)).

thought that a knowledge of the kinetics of oxidation of Fe(II)TPP by O<sub>2</sub> is essential if the complex is to be used as a catalyst in the LRSR process.

The oxidation rate of Fe(II)TPP in O<sub>2</sub>-saturated solutions at different pHs was determined by measuring the rate of Fe(II) disappearance and the experimental data are presented in Fig. 2. As can be seen, the kinetics of oxidation of Fe(II)TPP in the tris (pH 4) and borate buffered (pH 8) solutions can be described by Eq. (7). The R-squared values (R<sup>2</sup>) of the trend lines in Fig. 2 and Fig. S2 (SM) were between 98.9% and 99.9%, indicating that the mechanism of oxidation of Fe(II)TPP by O<sub>2</sub> can be described by reactions similar to Eq. (3)–(5) [26]. The kinetic parameters of the reaction between Fe(II)TPP and O<sub>2</sub> (*k*<sub>obs</sub>, *k*<sub>1</sub>, *k*<sub>2</sub>, and *K*<sub>eq</sub>) were calculated using the experimental data and the Fe(III)/Fe(II)TPP redox potential (see Brown and Mazzarella [26] for details), and the results are given in Table 1.

It is generally agreed that the rate of reaction of Fe(II) with O<sub>2</sub> is first-order with respect to the concentration of O<sub>2</sub>; however, its dependency on the Fe(II) concentration varies with varying concentration of Fe(II). Generally, authors reporting a second-order dependency on Fe(II) used high Fe(II) concentration, whereas a first-order dependency was observed at low Fe(II) dose [27]. A change from the first-order to the second-order dependency was also reported by Zang and Van Edlik [28] as they increased Fe(II) concentration. The results under our experimental conditions followed very well the mechanism proposed by Brown and Mazzarella [26], where the oxidation rate of Fe(II)TPP can, generally, be considered in a second-order dependency on the Fe(II) concentration. The *k*<sub>obs</sub> increased with increasing pH indicating the promoting effect of higher pH on the rate of reaction between Fe(II)TPP and O<sub>2</sub> and this agrees with the decreasing redox potential of Fe(III)/Fe(II)TPP with increasing pH (see Section 3.1). The *k*<sub>1</sub> value was found to be independent of pH within experimental errors and this is in accordance with the kinetics of oxidation of Fe(II)PDTA by O<sub>2</sub>. The decrease in *E*<sub>1/2</sub> of Fe(III)/(II)TPP with increasing pH makes the reduction of Fe(III)TPP to Fe(II)TPP by O<sub>2</sub> more difficult at high pH and this explains the decrease in *k*<sub>1</sub> value with increasing pH [26]. The value of *k*<sub>2</sub> decreased slightly with increasing pH, which also agrees with observations made by Brown and Mazzarella [26] and indicate that O<sub>2</sub><sup>•-</sup> is a poor oxidant at high pH values. The addition of Fe(III)TPP (or TPP into the Fe(II)TPP solution did not affect its rate of oxidation by O<sub>2</sub> (see Fig. S2e (SM)), in agreement with Sada, Kumazawa and Machida [29] who stated that the oxidation of Fe(II)NTA was not suppressed by the addition of excess of NTA. However, they have found that the oxidation of Fe(II)EDTA was inhibited by about 30% in the presence of 20% excess EDTA. The Fe(III)TPP did not have any effect on the oxidation of Fe(II)TPP by O<sub>2</sub> either, in accordance with Cher and Davidson [30] and Stumm and Lee [31].

### 3.3. The kinetics of O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III)TPP

The kinetics of O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III)TPP was investigated under O<sub>2</sub>-saturated conditions in the borate buffer solution at pH 9. In these tests, the concentration of catalyst

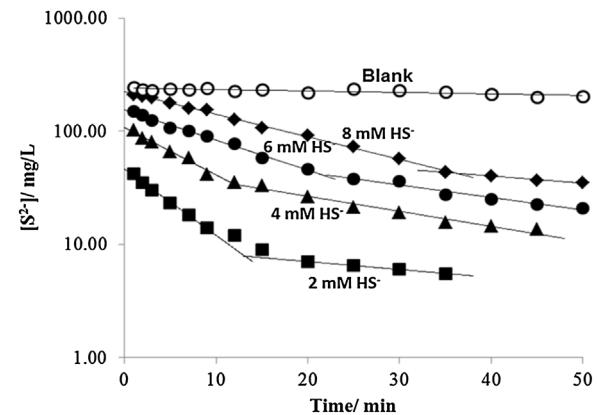


Fig. 3. The of O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III)TPP as a function of time for various initial HS<sup>-</sup> concentrations (pH = 9, [Fe(III)TPP]<sub>0</sub> = 0.5 mM, [HS<sup>-</sup>] = 2–8 mM).

(0.5 mM) was fixed while the concentration of HS<sup>-</sup> varied from about 2–8 mM. The time profile of the blank sample (HS<sup>-</sup> at 8 mM) presented in Fig. 3 shows that the rate of evaporation and oxidation of HS<sup>-</sup> by O<sub>2</sub> (*k* = 1.5 × 10<sup>-3</sup> M<sup>-1</sup>s<sup>-1</sup> [4]) is negligible during the oxygen gas sparging. The data presented in this figure also shows that HS<sup>-</sup> decay can be described by pseudo-first-order kinetics and that the decay profile appears to be, at least, biphasic. The first phase, which lasts about 10–30 min is attributed to Reactions (8) and (9), and the second phase is attributed to the formation of polysulfides, the intermediate products of oxidation of HS<sup>-</sup>, which are stronger nucleophiles than HS<sup>-</sup> and can compete effectively with the latter for the seventh coordination site in Fe(III)TPP in Reaction (8). The on-set of the second and slower reaction varies with varying initial concentration of HS<sup>-</sup> and shifts to longer time as the concentration of HS<sup>-</sup> increases. This is not unexpected because it will take longer time to deplete HS<sup>-</sup> and build-up adequate concentration of intermediate polysulfides that can compete with mono-sulfide for the seventh coordination site in Fe(III)TPP.

The air/O<sub>2</sub> oxidation of H<sub>2</sub>S catalyzed by Fe(III)EDTA [28] and Fe(III)NTA [29] was also reported to follow a pseudo-first-order. The reasons for these observations are discussed in the following section. The fraction of HS<sup>-</sup> oxidized in about 50 min was found to be about 92%, 90%, 89% and 86% for the initial concentration of about 2, 4, 6, and 8 mM, respectively.

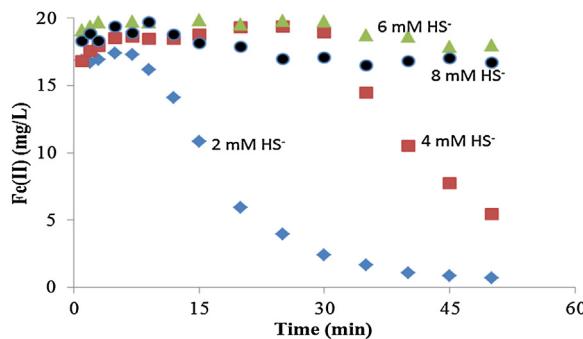
Fig. 4 presents the rate of generation of Fe(II) at various initial concentrations of HS<sup>-</sup>. As can be seen, Fe(II) is generated very fast and its concentration reaches a steady-state level almost instantaneously, stays at that level for sometimes, and then decays rapidly, when the majority of HS<sup>-</sup> and polysulfides are oxidized. The time span of Fe(II) steady-state concentration increases with increasing concentration of HS<sup>-</sup>. This is because the rate of oxidation of Fe(II)TPP by O<sub>2</sub>—the rate controlling step—and regeneration of Fe(III)TPP is considerably slower than the rate of reaction of Fe(III)TPP with HS<sup>-</sup>; and it takes longer and longer time to oxidize higher concentrations of HS<sup>-</sup>.

Table 1

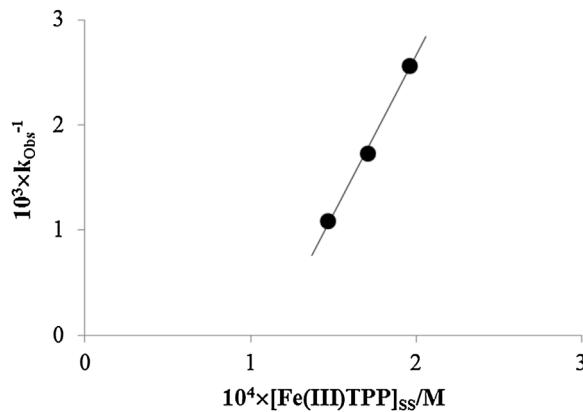
Kinetic parameters for the oxidation of Fe(II)TPP by O<sub>2</sub> at different pH ([Fe(II)]<sub>0</sub> = 0.5 mM and [TPP]:[Fe]<sub>0</sub> = 2:1).

|                   | pH  | 10 <sup>2</sup> <i>K</i> <sub>eq</sub> | <i>k</i> <sub>obs</sub> (s <sup>-1</sup> ) | 10 <sup>-4</sup> <i>k</i> <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> ) | 10 <sup>-3</sup> <i>k</i> <sub>1</sub> (M <sup>-1</sup> s <sup>-1</sup> ) | <i>k</i> <sub>1</sub> (M <sup>-1</sup> s <sup>-1</sup> ) |
|-------------------|-----|--|--|---|---|--|
| Phthalate buffers | 4.2 | 0.11                                   | 0.036 ± 0.007                              | 0.71 ± 0.14   | 2.77 ± 0.25   | 2.91 ± 0.26  |
|                   | 5   | 0.48                                   | 0.17 ± 0.013                               | 0.76 ± 0.056  | 2.50 ± 0.032  | 12.02 ± 0.15   |
|                   | 5.9 | 0.90                                   | 0.31 ± 0.004                               | 0.75 ± 0.010  | 1.49 ± 0.050  | 13.37 ± 4.45   |
| Tris buffer       | 7   | 2.37                                   | 0.41 ± 0.035                               | 0.38 ± 0.043  | 0.11 ± 0.0005   | 2.72 ± 0.012   |
|                   | 9   | 44.12                                  | 5.68 ± 0.049                               | 0.27 ± 0.007  | 0.022 ± 0.002   | 9.82 ± 1.03  |
| Borate buffers    |     |  |  |   |   |  |
|                   | 8   | 6.29                                   | 0.67 ± 0.068                               | 0.22 ± 0.023  | 0.031 ± 0.001   | 1.92 ± 0.08  |
|                   | 9   |  |  |   |   |  |

$$K_{eq} = k_1/k_{-1}, k_{obs} = \frac{4k_2 K_{eq} [O_2(\text{soln})]}{(1+R)} t$$



**Fig. 4.** The rate of generation of Fe(II) during the Fe(III)TPP catalyzed oxidation of HS<sup>-</sup> by O<sub>2</sub> at different initial HS<sup>-</sup> concentrations; pH = 9, [Fe(III)TPP]<sub>0</sub> = 0.5 mM, [HS<sup>-</sup>] = 2.8 mM.



**Fig. 5.** Plot showing the dependence of  $k'_{\text{obs}}$  on the steady-state concentration of Fe(III)TPP.

#### 3.4. The rate constant of the reaction between HS<sup>-</sup> and Fe(III)TPP

As described above, Fe(III)TPP is a catalyst that transfers electrons from HS<sup>-</sup> to O<sub>2</sub>; it reacts very fast with sulfhydryl ion and generates Fe(III)(HS<sup>-</sup>)TPP. This is followed by an electron transfer from HS<sup>-</sup> to Fe(III) and generation of HS<sup>•</sup> and Fe(II)TPP. The HS<sup>•</sup> dimerizes rapidly producing S<sub>2</sub><sup>2-</sup>, which in turn reacts with Fe(III)TPP and generates higher polysulfides. The Fe(II)TPP reacts with O<sub>2</sub> and oxidizes back to Fe(III)TPP. The rate of regeneration of Fe(III)TPP is slow – as compared to the rate of formation and dissociation of Fe(III)(HS<sup>-</sup>)TPP – and (as mentioned earlier) the rate determining step, leading to the quasi-steady-state concentration of both the Fe(III)TPP and Fe(II)TPP. This is demonstrated by the data presented in **Fig. 4**. The steady-state concentration of Fe(II)TPP increased from about 0.3 mM to about 0.33 mM as the concentration of HS<sup>-</sup> was increased from about 2 mM to 6 mM and stayed at that level with further increasing of HS<sup>-</sup> concentration. It is for these reasons that the rate of O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III) follows a pseudo-first-order kinetics. The rate of Reaction (8) under these conditions can be given by the following equation.

$$-\frac{d[HS^-]}{dt} = k_8 [HS^-] [Fe(III)TPP] = k'_{\text{obs}} [HS^-] \quad (10)$$

$$k'_{\text{obs}} = k [Fe(III)TPP]_{\text{ss}} \quad (11)$$

where [Fe(III)TPP]<sub>ss</sub> represents steady-state concentration of Fe(III)TPP.

**Fig. 5** shows that  $k'_{\text{obs}}$  varies linearly with varying steady-state concentration of Fe(III)TPP, from which a value of  $30.5 \pm 25.0 \text{ M}^{-1} \text{ s}^{-1}$  (with 95% confidence limit) was obtained for  $k_8$ . This value is more than an order magnitude higher than the previously reported value of  $0.8 \text{ M}^{-1} \text{ s}^{-1}$  [12], which was obtained by monitoring the rate of

growth of absorbance of Fe(III)(HS<sup>-</sup>)TPP at 611 nm within the first 40 s of the reaction. Therefore, the observed difference between the two values is not unexpected considering the complexity of the oxidation process and assumptions and approximations made for the derivation of  $k_8$  in the present work. Note that the  $k_8$  value is much lower than the rate constant of the reaction between Fe(III)EDTA and H<sub>2</sub>S ( $6.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  [4]) and this is attributed to the lower redox potential of Fe(III)/Fe(II)TPP at pH 9 ( $-0.14 \text{ V}$ ), resulting in a lower driving force for the oxidation of Fe(II)TPP by O<sub>2</sub> and regeneration of Fe(III)TPP.

#### 4. Conclusion

This study elucidated the kinetics of O<sub>2</sub> oxidation of HS<sup>-</sup> catalyzed by Fe(III)TPP as well as the kinetics of oxidation of Fe(II)TPP by O<sub>2</sub> and measured the half-wave reduction potential of Fe(III)/(II)TPP in different buffer solution and at different pH. The reduction potential of Fe(III)TPP confirmed that the complex is a suitable catalyst for the O<sub>2</sub> oxidation of H<sub>2</sub>S. The oxidation of Fe(II)TPP by O<sub>2</sub> was shown to follow a four-step mechanism proposed by previous researchers, and the reaction kinetic parameters at different pHs were calculated (employing experimental data) and provided. It has also been demonstrated that the catalyst forms a complex with HS<sup>-</sup> and by doing so shuttles electrons from the latter to molecular oxygen. The rate constant of the reaction of Fe(III)TPP with HS<sup>-</sup> was determined to be about  $30.5 \pm 25.0 \text{ M}^{-1} \text{ s}^{-1}$ . This value is more than an order of magnitude than the previously published data and this is attributed to the complexity of the reaction mechanism, assumptions and approximations made.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.06.040>.

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